Research Summary: Clay nanocomposite and polyelectrolyte multilayers assemblies

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Layered silicate nano-composites are rapidly becoming an important commercial source of materials for low gas and vapor permeability barriers. Some clay/polymer composites have been shown experimentally to offer significantly reduced permeabilities over the individual polymer materials. This can be explained partly by the added tortuosity of the path that a gas molecule or atom must take to transverse the polymeric nanocomposite membrane due to the combination of crystalline (clay) and amorphous (polymer) regions. Lately the research in this area has taken a new direction: the fabrication of polyelectrolyte multilayers via electrostatic self-assembly. The latter method has the advantage of being much simpler and cost-effective for preparing thin films. However, its drawback is the extensive interpenetration between neighboring layers affecting the internal order.

To gain a better insight into the properties these composite systems exhibit, molecular modeling -together with the various computational methods it involves- provides a very valuable tool. By employing these methodologies, extended information on the intercalation kinetics of the polymers inside the clay, structural and transport properties may be obtained.

One of the first steps to be pursued in molecular modeling is the development of a force field that contains parameters that proper characterize the physical interactions between the component atoms that form the model. For the case of nanocomposite systems, these interactions are separated into three constituent parts: inorganic-inorganic (mineral), organic-organic (polymer) and inorganic-organic. The present force field version used to model nanocomposites combines the Morse-Stretch Charge Equilibration Force Field (MSQ) for the inorganic components [1] and the Dreiding Force Field for the organic component [2]. The mixed non-bond organic-inorganic interactions (electrostatic and van der Waals) were separately calculated and added. One of the important features of this combined force field is that the atomic charges are allowed to readjust instantaneously to the atomic configurations. These charges are calculated using the charge equilibration (QEQ) method [3].

To test this force field a series of layered clay minerals (mostly of 2:1 type[1]) were build from X-ray diffraction data. The force field predicted structure of these clays was obtained by minimization applying certain convergence criteria (the Root-mean Square force on the atoms had to converge to a value as small as 10^{-2} kcal mol^{-1} Å and the maximum displacement of the atoms corresponding to one minimization step was set to 0.2Å). The cell parameters and angles, volume and density of the unit cell were compared between the original X-ray structure and the predicted one. Additionally, the Root-mean Square and maximum displacement of all the atoms in the structure was calculated and also the group symmetry was recalculated. With few exceptions, the original (crystallographic) symmetry was recovered and small displacements of the atoms were observed. Where large values of RMSD were calculated, they could be assigned to the movement of hydrogens (X-ray diffraction data do not provide information on the position of hydrogens). For layered clays a key parameter is the interlayer distance which is for most structures available experimentally. Again, our predictions are in very good agreement with experiments.

In our study, the clay of interest to form clay nanocomposites is montmorillonite (MMT). MMT is a 2:1 clay mineral with an interlayer distance of 9.6 Å. Usually pristine clays have a negative charge distributed over the layer surface. Thus, a neutral structure will always require a

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[1] A 2:1 clay mineral is a sandwich structure of two tetrahedral and one octahedral layer. The tetrahedral sheets mostly contain silica while the octahedra are formed of aluminum and magnesium oxygen-hydroxyl.

certain number of counter-ions to be present in the interlayer to compensate for the negative charge. The number of charges present in the interlayer define de Cation Exchange Capacity that is a characteristic of different clays. The MMT structure that we model has six sodium (Na+) counter-ions in the interlayer that corresponds to a CEC of 0.95 meq g^{-1}.

From the energetic point of view a characteristic property of a material is the cohesive energy (the energy to completely evaporate the system). However, for clay materials it is more meaningful to think of the equivalent surface energy: the energy required to split the structure in a perpendicular direction to the interlayer gap (i. e., to open an infinite gap). The calculated surface energies for the hydrated structures are in very good agreement with experimental data. For example, the experimental range for the surface energy of hydrated mica is between 130-170 dyne cm^{-1} while our predicted value is 105 dyne cm^{-1}. For both anhydrous and hydrated MMT, the surface energies are larger than for mica. This suggests that mica may be a better candidate than MMT to form nanocomposites.

To ease the intercalation of polymers in the gallery of the clays, very often the counterions are replaced by organic surfactants. The organic surfactants (alkyl-ammonium is one of the most frequent used surfactant) influence the future process of polymer intercalation by:

- increasing the interlayer distance between the clay sheets;
- lower the surface energy of the clay;
- favoring the non-polar interactions.

In our molecular dynamics study we investigate the effect of a variable number of carbons in the alkyl-ammonium tail (n) on the interlayer distance. Our calculations indicate that there is a transition from monolayer to bi-layer of the confined alkyl-ammonium chains when n increases from 10 to 12. This transition also corresponds to an increase of about 3 Å in the interlayer distance of the clay. These results are in very good agreement with experimental data on similar systems. The calculated binding energies of alkyl-ammonium (variable n) in MMT indicate that the most stable systems are those formed for n=6 and n=16 while the most unstable one corresponds to n=12. Thus, for polymer intercalation the dodecyl-ammonium would provide the most favorable environment.

Dynamics calculations for polymer-surfactant-clay systems offer information on the interfacial interaction, kinetic of confinement of the polymer in the interlayer of the clay. From these calculations enough information can be extracted on the void and channel distribution inside the system to perform Kinetic Monte Carlo calculations and estimate the diffusion and permeability properties of nanocomposites.

For the polyelectrolyte multilayers, our calculations on the height of a repeating unit for a combination of MMT and PDDA already give good agreement with the available experimental information. Our next focus will be to study the effect partial replacements of interlayer cations with PDDA will have on the structural and dynamic properties of these assemblies.

References:

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